U. S. NAVY
OFFICE OF NAVAL RESEARCH
Research Contract N7onr-32912
Project NR 092 162

STUDIES ON THE PHOTOCHEMICAL SYNTHESIS OF HYDRAZINE AND OTHER ENDOTHERMIC SUBSTANCES

Status Report

for the period 15 February to 15 April 1954

by

Harry E. Gunning

with

C. Luner and C. C. McDonald

Illinois Institute of Technology
Department of Chemistry
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A. THE PHOTOCHEMICAL SYNTHESIS OF HYDRAZINE FROM AMMONIA

A paper based on our fundamental studies of the mechanism of hydrazine formation in the photolysis of ammonia under flow conditions at 1849 Å has been accepted for publication in the Journal of Chemical Physics. It is scheduled to appear in the May issue of the journal. A second paper dealing with the results of our investigation of the mechanism of hydrazine synthesis in the mercury-6($^3P_1$)-photosensitized decomposition of ammonia is nearing completion. The manuscript will be submitted shortly to the aforementioned journal.

B. STUDIES ON THE FACTORS WHICH INFLUENCE THE INTENSITY AND EFFICIENCY OF MERCURY RESONANCE SOURCES

The total output of the Hanovia Biosteritron source has been measured using a uranyl oxalate actinometer coupled with a Hanovia ultraviolet meter. A maximum output of 1.9×10^{-3} einstein per minute was obtained at 100 ma and 1200 volts. Maximum efficiency occurs at much lower intensities. A custom-made quartz resonance lamp consisting of a six-coil helix, each coil 5.5 cm. I.D. and fashioned of 10 mm. I.D. tubing, was found to give approximately the same intensity per unit area of radiating surface as the Biosteritron source.

An electrodeless discharge source consisting of a straight quartz tube, 19 cm. in length and 15 mm. I.D., was selected for measurements on this type of lamp. The discharge was excited and maintained by tuning the lamp to a 27.12 megacycle oscillator. At maximum intensity and a current

of 100 ma, the measured total output of the lamp was found to be 0.072×10^{-3} einstein per minute--a much lower value than those obtained for the electroded lamps. However, it should be emphasized that these conditions do not represent a true measure of the efficiency of such sources, since loss of R.F. energy is very high for the defined system. More efficient coupling, using a resonant cavity, would undoubtedly lead to much higher intensities.

C. THE MERCURY-6($^3P_1$)-PHOTOSENSITIZED DECOMPOSITION OF ETHYLENEIMINE

This reaction is being studied in detail since it offers the possibility of forming highly endothermic products by radical recombination. The products of the reaction for the static system have been identified by mass spectrometric techniques. Data on the rates of formation of products as a function of both substrate pressure and time are being accumulated. These data, coupled with our measurements of the incident light intensity, can be used for calculating quantum yields. It is expected that sufficient material for a publication on the static decomposition will have been obtained by the end of the present contract period. The detailed results of the investigation will be included in our next technical report. Primary products of the reaction will be ascertained by studies of the reaction under flow conditions, in a manner similar to that used in the hydrazine studies.

D. THE MERCURY-6($^3P_1$)-PHOTOSENSITIZED DECOMPOSITION OF BORON TRICHLORIDE

A number of flow runs have been made on the reaction of boron trichloride with Hg $6(^3P_1)$ atoms. The decomposition takes place rather readily with the concommitant formation of calomel. Other studies in this laboratory have shown that the calomel arises in this reaction by the interaction of chlorine atoms with normal mercury atoms. In short, the primary process apparently involves the formation of BCl_2 radicals and chlorine

atoms. No calomel seems to form in the collision between the photoexcited mercury atoms and the boron trichloride. A liquid product has been isolated from the reaction; however, its chemical identity has not yet been established. Since the boron trichloride used contained a small amount of phosgene, which could not be removed by repeated distillations in vacuo, it is possible that the liquid product might contain contaminating products from the phosgene reaction.

E. THE PHOTODECOMPOSITION OF TITANIUM TETRACHLORIDE

Apparatus is in process of construction for studying the photochemistry of $TiCl_4$. This molecule offers rather interesting possibilities for the photochemical synthesis of endothermic substances such as $TiCl_3$ and $TiCl_2$. It will be necessary to obtain data on the absorption spectrum of the tetrachloride before the most suitable system for photochemically initiating the reaction can be established. It should, however, be noted that both the trichloride and the dichloride are solids, and consequently it is contemplated that the problem of removing the products from the reaction zone should be considerably easier than in the removal of hydrazine from the ammonia stream in the ammonia reaction.

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